

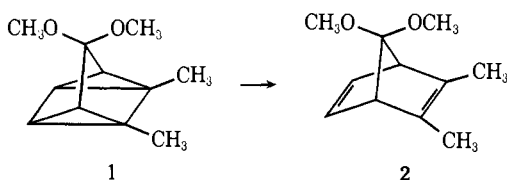
Transition Metal Complex Promoted Isomerizations. Rhodium(I) Complex Promoted Rearrangements of Methylated Bicyclo[1.1.0]butanes^{1,2}

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Abstract: The transition metal complex promoted isomerizations of 1,2,2-trimethylbicyclo[1.1.0]butane, 1,2,2,3-tetramethylbicyclo[1.1.0]butane, and 2,2,4,4-tetramethylbicyclo[1.1.0]butane have been studied. Rhodium(I), in the form of different derivatives, promoted the isomerization of simple bicyclo[1.1.0]butanes to derivatives of 1,3-butadiene or derivatives of vinylcyclopropane. Through the use of 3-deuterio-1,2,2-trimethylbicyclo[1.1.0]butane and rhodium dicarbonyl chloride dimer, it was established that the isomerization to 1,3-butadiene derivatives involved cleavage of a side bond and the center bond of the bicyclo[1.1.0]butane nucleus in a *formal* retrocarbene addition. Detailed studies indicated that the cleavage process was most likely a stepwise process in which a side bond was cleaved, followed by subsequent cleavage of the center bond. The intermediate generated at this stage is best described in terms of a resonance hybrid of a transition metal complexed carbene-transition metal bonded carbonium ion. The effect of varying the methyl substitution pattern on the mode of cleavage of the bicyclo[1.1.0]butane nucleus is discussed. In the case of 2,2,4,4-tetramethylbicyclo[1.1.0]butane, where a 1,3-butadiene cannot be derived from a simple hydrogen migration, a vinyl migration is suggested. The feasibility of such a vinyl migration was supported by a study of the transition metal complex promoted rearrangement of homoallylic diazoalkanes in which a formal vinyl migration is shown to be the exclusive mode of reaction. The mode of cleavage of the methylated bicyclo[1.1.0]butanes was shown to be dependent on the nature of the transition metal complex and on the nature of the groups attached to the bicyclo[1.1.0]butane nucleus. The mechanistic aspects of these rearrangements are discussed.

In a completely serendipitous manner, we discovered that certain metal complexes promoted the rearrangement of quadricyclanes to norbornadienes.^{3,4} The discovery that **1** was thermally stable to 200°,



but reverted to **2** in seconds at low temperature in the presence of certain transition metal complexes, came as a surprise. We associated the lability of **1** in the presence of transition metal complexes to the 95 kcal/mol of strain energy⁹ incorporated in the quadricyclane

skeleton. This raised the question of whether less strained ring systems,^{9,10} such as bicyclo[1.1.0]butane and bicyclo[2.1.0]pentane, which have strain energies of *ca.* 66 and 54 kcal/mol, respectively, would be susceptible to transition metal complex promoted rearrangement.¹¹ We now wish to report the results of our investigation of this problem, relative to simple methylated derivatives of bicyclo[1.1.0]butane.

Before discussing the reaction of derivatives of bicyclo[1.1.0]butane with transition metal complexes, it is necessary to quickly review certain aspects of the related thermal chemistry. The thermal isomerizations of **3** to a mixture of **4** and **5**,^{12,13} and of **6**¹⁴ to **7**, are typical examples of the thermal behavior of bicyclo[1.1.0]butanes. Many different research groups have explored this type of thermal chemistry¹⁵ and the mech-

(1) Paper XXXII on The Chemistry of Bent Bonds. For the previous papers in this series see P. G. Gassman and T. Nakai, *J. Amer. Chem. Soc.*, **93**, 5897 (1971); P. G. Gassman and F. J. Williams, *Chem. Commun.*, 80 (1972); P. G. Gassman and R. P. Thummel, *J. Amer. Chem. Soc.*, **94**, 7183 (1972); P. G. Gassman and W. J. Greenlee, *Syn. Commun.*, in press.

(2) For preliminary reports of parts of this investigation see (a) P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **92**, 7631 (1970); (b) P. G. Gassman, T. J. Atkins, and F. J. Williams, *ibid.*, **93**, 1812 (1971).

(3) P. G. Gassman and D. S. Patton, *ibid.*, **90**, 7276 (1968); P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **90**, 7271 (1968).

(4) In a completely independent study Hogeveen and Volger⁵ also reported on this facile isomerization of quadricyclanes to norbornadienes. However, an unrecognized example of this type of isomerization had been observed by Cristol and Snell much earlier.⁶ Various mechanistic interpretations of the basis for these rearrangements have appeared.^{7,8}

(5) H. Hogeveen and H. C. Volger, *J. Amer. Chem. Soc.*, **89**, 2486 (1967).

(6) S. J. Cristol and R. L. Snell, *ibid.*, **80**, 1950 (1958).

(7) F. D. Mango and J. H. Schachtschneider, *ibid.*, **89**, 2484 (1967); **93**, 1123 (1971).

(8) L. Cassar and J. Halpern, *Chem. Commun.*, 1082 (1970).

(9) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968).

(10) For various recent discussions of strain in polycyclic molecules see N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); P. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970); S. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *ibid.*, **92**, 3109 (1970); N. C. Baird, *Tetrahedron*, **26**, 2185 (1970).

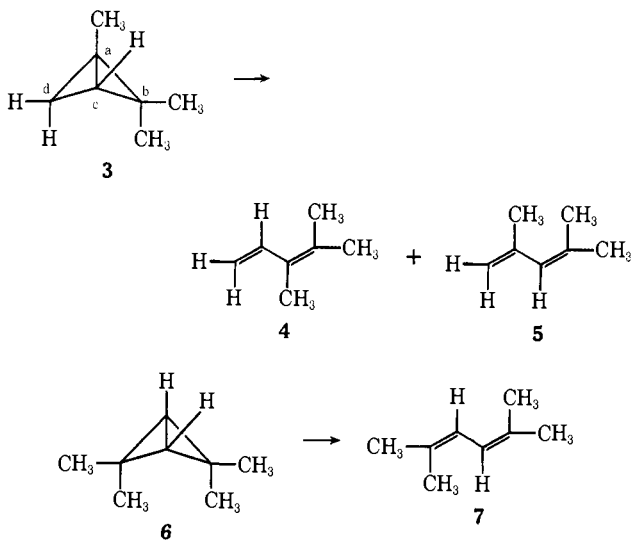
(11) In a series of papers starting in 1967, Pettit and coworkers have shown that molecules containing at least three fused four-membered rings are readily isomerized by silver ion and cuprous ion: W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 4788 (1967); J. Wristers, L. Brenner, and R. Pettit, *ibid.*, **92**, 7499 (1970). Recently, the use of Pettit's silver ion catalyzed rearrangement of fused cyclobutanes has been extended to cube type molecules: W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. J. Palmer, *Tetrahedron Lett.*, 787 (1970); L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584 (1970).

(12) L. Skattebøl, *Tetrahedron Lett.*, 2361 (1970).

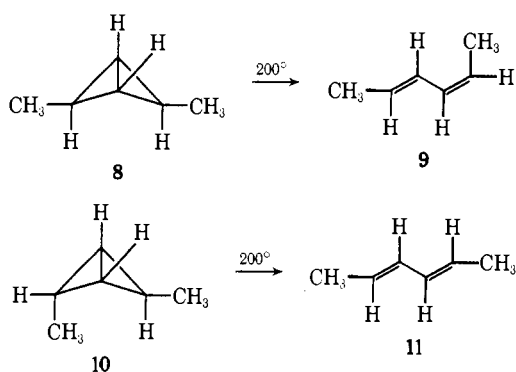
(13) W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, *ibid.*, 2365 (1970).

(14) For the preparation of **6** see H. K. Hall, Jr., C. D. Smith, E. P. Blanchard, Jr., S. C. Cherkofsky, and J. B. Siega, *J. Amer. Chem. Soc.*, **93**, 121 (1971). We wish to thank Dr. Cherkofsky for providing us with the experimental procedure for the preparation of **6** prior to publication.

(15) (a) W. Mahler, *J. Amer. Chem. Soc.*, **84**, 4600 (1962); (b) D. M. Lemal, F. Menger, and G. W. Clark, *ibid.*, **85**, 2529 (1963); (c) K. B. Wiberg and G. M. Lampman, *Tetrahedron Lett.*, 2173 (1963); (d) J. P. Chesick, *J. Phys. Chem.*, **68**, 2033 (1964); (e) R. Srinivasan, A. A. Levi,



anism of these thermal isomerizations has been discussed in detail.^{15m, 15o, 16, 17} In spite of the relatively large strain energy incorporated in the bicyclo[1.1.0]butane nucleus, temperatures of 150–300° and activation energies in excess of 40 kcal/mol^{15d, 15g} are required for a reasonable rate of isomerization. These thermal rearrangements are readily rationalized in terms of the concerted cleavage of two of the side bonds of the bicyclo[1.1.0]butane nucleus.¹⁷ Relatively definitive evidence for the intervention of a concerted process was provided by Closs and Pfeffer,^{16c} who demonstrated that **8** gave 93% of **9**, while **10** thermolyzed to give



95% of **11**. These rearrangements required that one cyclopropyl ring cleave in a conrotatory manner while the other cleave in a disrotatory fashion. The findings of Closs and Pfeffer leave no doubt concerning the lack of thermal cleavage of the central bond of the bi-

and I. Haller, *ibid.*, **69**, 1775 (1965); (f) H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 144 (1964); (g) H. M. Frey and I. D. R. Stevens, *Trans. Faraday Soc.*, **61**, 90 (1965); (h) A. Small, *J. Amer. Chem. Soc.*, **86**, 2091 (1964); *J. Org. Chem.*, **33**, 1441 (1968); (i) W. von E. Doering and J. F. Coburn, Jr., *Tetrahedron Lett.*, 991 (1965); (j) S. Masamune, *ibid.*, 945 (1965); (k) E. P. Blanchard, Jr., and A. Cairncross, *J. Amer. Chem. Soc.*, **88**, 487, 496 (1966); (l) J. Pusset and R. Beugelmans, *Tetrahedron Lett.*, 3249 (1967); (m) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968); (n) D. P. G. Hamon, *ibid.*, **90**, 4513 (1968); (o) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); K. B. Wiberg, *Advan. Alicycl. Chem.*, **2**, 185 (1968); (p) R. B. Woodward and D. L. Dalrymple, *J. Amer. Chem. Soc.*, **91**, 4612 (1969); I. A. D'yakov, V. V. Razin, and M. I. Komendantov, *Tetrahedron Lett.*, 1127, 1135 (1966).

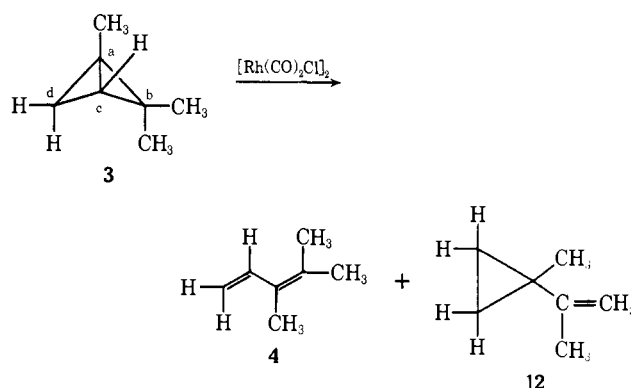
(16) (a) K. B. Wiberg and J. M. Lavanish, *J. Amer. Chem. Soc.*, **88**, 5272 (1966); (b) K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968); (c) G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, **90**, 2452 (1968).

(17) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969). In particular see pp 810–814.

cyclo[1.1.0]butane nucleus in the thermal conversion of bicyclo[1.1.0]butanes to butadienes. Applying the concepts of Closs and Pfeffer to the thermal isomerization of **3**, it can be seen that **4** resulted from concerted cleavage of the a–d and b–c bonds, while **5** was derived from a similar cleavage of the a–b and c–d bonds of **3**.

Rhodium Dicarbonyl Chloride Dimer Promoted Isomerizations

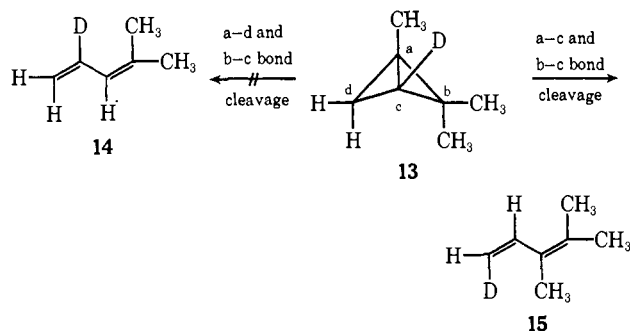
When **3** was treated with 3 mol % of rhodium dicarbonyl chloride dimer in chloroform at 25°, an immediate exothermic reaction occurred which yielded, after 5 min, 58% of **4** and 30% of **12**. The structures



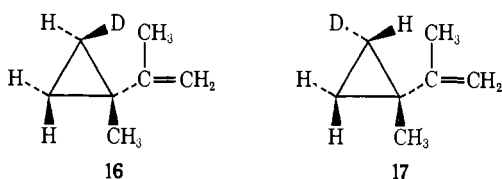
of **4** and **12** were established through a combination of infrared, ultraviolet, and nmr spectroscopy. In addition, **4** was catalytically reduced to 2,3-dimethylpentane which was identical with an authentic sample. Similarly, **12** was compared with an authentic sample prepared by an alternate route.^{12, 13} On the surface it would appear that the transition metal complex was facilitating one part of the thermal rearrangement, while completely neglecting the other. In addition, it seemed that even part of this preferred process was being interrupted at a preliminary stage to produce the vinylcyclopropane derivative, **12**. Careful consideration of possible routes from **3** to **4** indicated that two plausible processes merited consideration. One was the close analogy to the thermal process in which the a–d and b–c bonds of **3** would cleave to give **4** directly. The alternate process involved cleavage of the a–c and b–c bonds of **3**, followed by hydrogen shift. Using the principle of Occam's Razor,¹⁸ the second possible mechanism, being much more complex than the first, would be discarded. However, having little faith in the value of Occam's Razor,¹⁸ we decided to test these alternate possibilities. When **3** was treated with butyllithium¹⁹ followed by neutralization with deuterium oxide, the hydrogen at the bridgehead was replaced by deuterium (ca. 80–85% deuterium incorporation by nmr analysis) to give **13**. Cleavage of the a–d and b–c bonds of **13** via metal complexes would give **14**, while the alternate process of cleavage of the a–c and b–c bonds, followed by hydrogen shift, would produce **15** (or the isomer with the deuterium trans). When a

(18) Named for William of Ockham, 14th century English scholastic philosopher. In its simplest terms, Occam's Razor decrees that a simple explanation is accepted in preference to a complex explanation. It is our opinion that, in the hands of a mechanistic chemist, Occam's Razor is often a dull tool.

(19) For a discussion of the acidity of the bridgehead hydrogens of bicyclo[1.1.0]butanes, see G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 2022 (1963); G. L. Closs and R. B. Larrabee, *Tetrahedron Lett.*, 287 (1965).



solution of **13** in chloroform was treated with 3 mol % of rhodium dicarbonyl chloride dimer at 25°, we obtained **15** as the only diene product. Within the limits of analysis by nmr spectroscopy, the process was amazingly stereospecific. None of the isomer with the deuterium trans to the vinyl substituent could be detected. In addition to **15**, we obtained the expected amount of **16**.



The structure of **15** was established on the basis of a comparison of the nmr spectra of **15** and **4**. As shown in Figure 1, the nmr spectrum of **4** consisted of two overlapping singlets at τ 8.26 and 8.22 (9 H) for the three methyl groups, a one-proton doublet (H_B) at τ 5.10 ($J_{AB} = 11$ Hz), a one-proton doublet (H_C) at τ 4.95 ($J_{AC} = 17$ Hz),²⁰ and a one-proton doublet of doublets (H_A) at τ 3.20. The diene **15** gave an nmr spectrum which showed no change in the pattern for the methyl groups. However, the pattern for H_A changed to a well-defined doublet of triplets at τ 3.20 ($J_{AB} = 11$ Hz, $J_{HD} = 2.8$ Hz²¹), H_B appeared as a one-proton doublet at τ 5.10, and H_C , which had been replaced to the extent of *ca.* 80% with deuterium, appeared as a doublet at τ 4.95 with only 18% of its former intensity. This spectral comparison firmly established that the deuterium was at the 1 position of **15** and that the stereochemistry about the C_1 - C_2 double bond had the *Z* configuration.²² The structure of the vinylicyclopropane derivative was established as **16** on the basis of a comparison of the nmr spectra of **12**, **16**, and **17**.²³ Whereas **12** showed the proton resonances of the hydrogens on the ring as a pair of two-proton multiplets at τ 9.33 and 9.59, **16** gave a two-proton absorption at τ 9.33 and a 1.1-proton absorption at τ 9.59. In comparison, **17**, whose structure had previously been established,¹³ showed a one-proton absorption at τ 9.33 and a two-proton absorption at τ 9.59.

(20) Normal ranges for J_{AB} , J_{AC} , and J_{BC} are 6–14 Hz, 11–18 Hz, and 0–3.5 Hz, respectively (L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p 85).

(21) H. J. Bernstein and N. Sheppard [*J. Chem. Phys.*, **37**, 3012 (1962)] have shown that $J_{HH} \cong 6.55J_{HD}$. On the basis of a J_{HH} of 17 Hz, a value of 2.6 Hz would have been predicted for J_{HD} in our system.

(22) For a discussion of this nomenclature see: J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968).

(23) We wish to thank Professor W. R. Moore for providing an nmr spectrum of **17**.

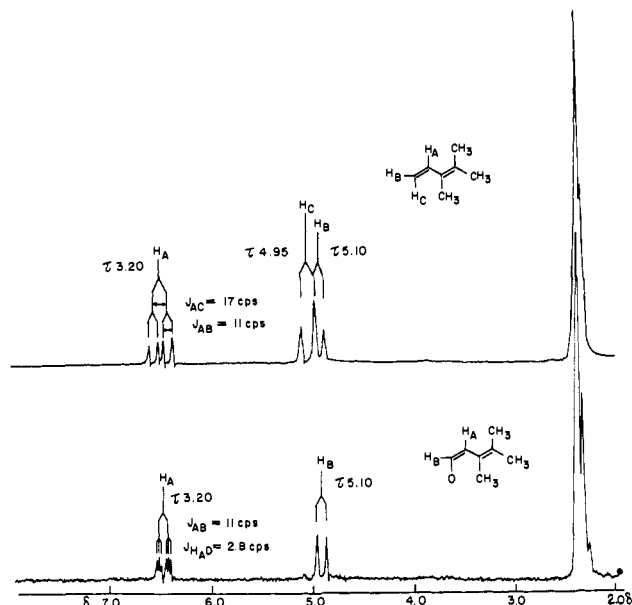
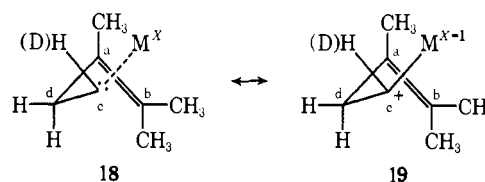


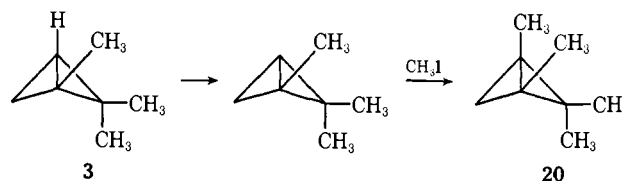
Figure 1. 100-MHz nmr spectra of **4** (top) and **15** (bottom).

The formation of **15** in the rhodium dicarbonyl chloride promoted isomerization of **13** firmly established that the reaction involved cleavage of the a-c and b-c bonds. Overall, this process can be envisaged as a *formal* retrocarbene addition. In more detailed consideration, we feel that the cleavage of these two bonds leads to an intermediate which is a resonance hybrid of a metal-complexed carbene **18** and a metal-



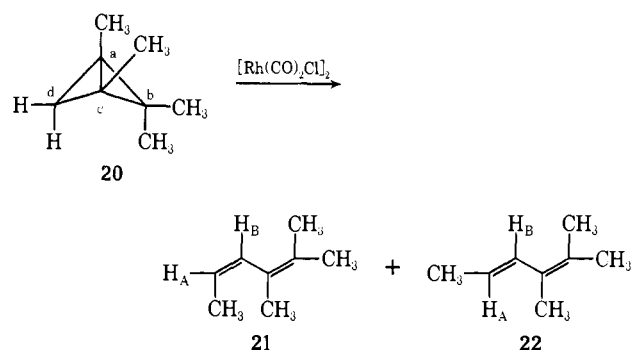
bonded carbonium ion **19**. Transfer of a hydrogen from C_d to C_c accompanied by loss of M^X would then produce the observed product. Our suggestion that a resonance hybrid of **18** and **19** represents a reasonable picture of the intermediate formed in these metal complex promoted rearrangements does not require that the a-c and b-c bonds break simultaneously. In fact, we feel that the cleavage of these bonds involves a stepwise process in which the b-c bond is broken first (*vide post*). Such a stepwise process would readily explain the formation of vinylicyclopropane derivatives as minor products.

Treatment of **3** with *n*-butyllithium-tetramethylethylenediamine in ether followed by methyl iodide gave **20**.¹³ When this tetramethylated bicyclo[1.1.0]-



butane was treated with 5 mol % of rhodium dicarbonyl chloride dimer in chloroform at room temperature, no detectable amounts of **20** remained after 5 min. In the presence of the metal complex, **20** was rapidly

isomerized to yield 46% of **21** and 50% of **22**.²⁴ Again,



the transition metal complex promoted the cleavage of one side bond (a-b or b-c) and of the central bond (a-c) in a process which could be viewed as a *formal* retrocarbene addition, followed by a hydrogen shift. The structures of **21** and **22** were established on the basis of both chemical and spectroscopic evidence.

Both **21** and **22** were readily hydrogenated to yield 2,3-dimethylhexane, which was identical with a commercial sample.²⁵ The stereochemistry of **21** and **22** was established on the basis of both nmr and uv spectroscopic data. Diene **22** showed a normal uv maximum at $\lambda_{\text{max}}^{\text{isooctane}}$ 240 nm (ϵ 17,750). In contrast, **21** gave an abnormal uv spectrum with $\lambda_{\text{max}}^{\text{isooctane}}$ 220 nm (ϵ 3850). This short wavelength, low extinction coefficient absorption was consistent with expectations for a twisted diene. Diene **21** would be expected to have strong methyl-methyl interactions which would prevent the double bonds from achieving coplanarity. This lack of coplanarity would be expected to decrease orbital overlap. Thus, **21** would be expected to resemble a twisted diene such as 1,3-cyclooctadiene, $\lambda_{\text{max}}^{\text{isooctane}}$ 228 nm (ϵ 4300). The nmr spectrum of **21** showed H_A at τ 4.63 and H_B at 4.12 with $J_{AB} = 11$ Hz.²⁶ In comparison, **22** had H_A at τ 4.54 and H_B at 3.56 with $J_{AB} = 15$ Hz.²⁶ Both the positions of the proton resonances and the larger coupling constant between the vinylic protons of **22** were consistent with the assigned structures.

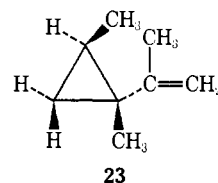
It should be noted that the presence of the additional bridgehead methyl group significantly changed both the course and specificity of the isomerization of **3** (and **13**). Whereas **3** isomerized stereospecifically to give only a single diene, as demonstrated by the conversion of **13** to **15**, the rearrangement of **20** occurred in a nonstereospecific manner to yield an almost statistical mixture of **21** and **22**. Furthermore, while both **3** and **13** gave significant amounts of vinylcyclopropane in a stereospecific manner, as illustrated by the formation of **16** from **13**, the rhodium dicarbonyl chloride dimer promoted catalyzed rearrangement of **20** gave no detectable amounts of **23**²⁷ or its epimer. In control experiments, it was demonstrated that **23**

(24) Both **21** and **22** were previously reported in the literature as a mixture: D. F. Schneider and C. F. Garbers, *J. Chem. Soc.*, 2465 (1964).

(25) Purchased from Chemical Samples Co., Columbus, Ohio.

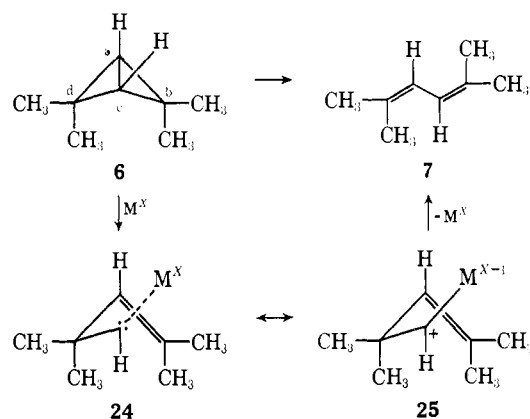
(26) H_A was also coupled with the terminal methyl group in both **21** and **22** with $J = 6.5$ Hz.

(27) By analogy to the formation of **16** from **13**, any vinylcyclopropane formed from **20** would be expected to have the stereochemistry shown by **23**. For the verification of this hypothesis and the preparation of **23** see P. G. Gassman, G. R. Meyer, and F. J. Williams, *J. Amer. Chem. Soc.*, **94**, 7741 (1972).



was not isomerized to either **21** or **22** by rhodium dicarbonyl chloride dimer under the reaction conditions.

Since the rhodium dicarbonyl chloride promoted isomerizations of **3**, **13**, and **20** all involved a hydrogen migration from C_a to C_c , we next decided to investigate the rearrangement of a bicyclo[1.1.0]butane which lacked the requisite migratable hydrogen. For this purpose we chose 2,2,4,4-tetramethylbicyclo[1.1.0]butane (**6**).¹⁴ When **6** was treated with 5 mol % of rhodium dicarbonyl chloride dimer at 25° in chloroform for 5 min, an 83% yield of **7** was obtained. The structure of **7** was established on the basis of its characteristic nmr and uv spectra and *via* comparison with an authentic sample.²⁵ Superficially the formation of **7** from **6** would appear to be occurring by way of cleavage of the side bonds (either a-b and c-d, or a-d and b-c) and not *via* breakage of the center bond (a-c). In this manner, the rearrangement would seem to be analogous to the thermal isomerization of **6**. However, the cleavage of only side bonds would be quite inconsistent with the precedent set by the rhodium dicarbonyl chloride dimer promoted isomerizations of **3**, **13**, and **20**. For this reason we decided to investigate other possible mechanistic routes from **6** to **7**. An explanation consistent with our previous findings would involve cleavage of the a-c and b-c bonds of **6** to yield a resonance hybrid represented by the metal-complexed carbene, **24**, and the metal-bonded carbenium ion, **25**, as resonance contributors.

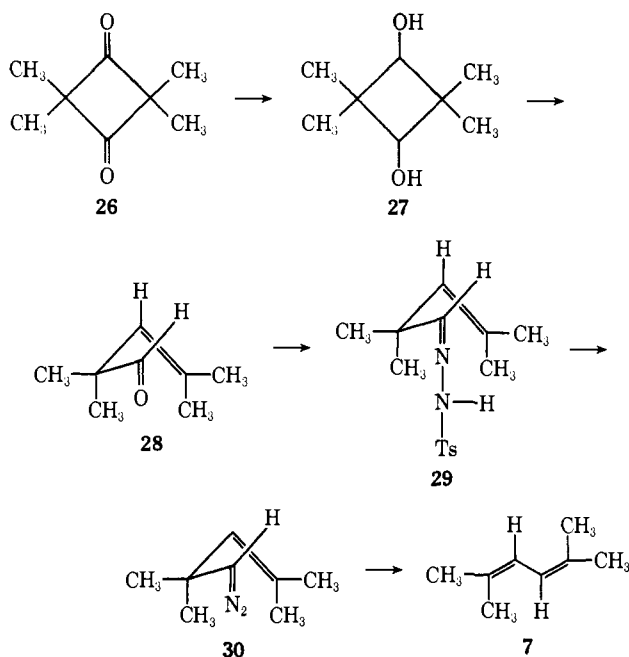


It has been shown that migratory aptitudes to a carbenoid center are hydrogen > vinyl > methyl.²⁸ Since the **24** \rightarrow **25** hybrid lacks the adjacent hydrogen preferred for migration, the choice is between a vinylic moiety and a methyl group. The shift of the vinylic moiety should be preferred on the basis of migratory aptitudes. This migration of the vinyl portion of the molecule would result in the formation of **7**.

Unfortunately, the high degree of symmetry incorporated in both **6** and **7** makes a definitive test of the

(28) Professor H. Shechter and Dr. A. Kraska, private communication. We wish to thank Professor Shechter and Dr. Kraska for enlightening and helpful discussions and for providing us with this information prior to publication.

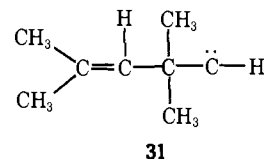
two alternate mechanisms discussed above impossible. However, evidence for the feasibility of the formation of the **24**–**25** hybrid could be obtained. Commercial dimethylketene dimer **26** was readily reduced to the



diol **27**, which on treatment with acid according to the literature procedure gave 2,2,4-trimethylpent-3-enal (**28**).²⁹ The tosylhydrazone **29** was readily obtained through reaction of **28** with *p*-toluenesulfonylhydrazine in methanol. Addition of butyllithium to a solution of **29** in tetrahydrofuran gave the lithium salt of **29**. The solvent was removed to give the crystalline salt which was transferred to a vacuum line. Evacuation of the system to 0.003 mm followed by heating of the tosylhydrazone salt to 85–90° produced decomposition of the tosylhydrazone salt and generated the diazo compound **30** which was collected in a trap at –70°. Within the limits of analysis by ir and nmr spectroscopy, the only contaminant present in the diazo compound was some residual tetrahydrofuran. Addition of trace amounts of rhodium dicarbonyl chloride dimer to the mixture of **30** and tetrahydrofuran caused an immediate exothermic reaction accompanied by vigorous evolution of nitrogen. Within seconds, **30** was completely decomposed. Vpc, ir, and nmr analysis indicated that *the only product formed in the rhodium dicarbonyl chloride dimer promoted decomposition of 30 was 7*. This is to be contrasted with the thermal decomposition of **30** which gave a mixture consisting of at least seven products.²⁸

The significant difference in the products formed in the thermal *vs.* the transition metal promoted reaction of **30** indicated that rhodium dicarbonyl chloride dimer was serving as more than just a catalyst for the conversion of **30** into the noncomplexed carbene **31**. The observed behavior strongly suggested that **30** reacted with the rhodium dicarbonyl chloride dimer to give an intermediate which is best represented as a resonance hybrid of **24** and **25**. The formation of **7** from **30** through the intermediacy of **24** ↔ **25** and of **7** from **6** does not require that the conversion of **6** into **7** also proceed

(29) R. H. Hasek, R. D. Clark, and J. H. Chaudet, *J. Org. Chem.*, **26**, 3130 (1961).



via the intermediacy of **24** ↔ **25**; it only indicates the reasonable nature of such a postulate.³⁰

Throughout the discussion presented above, we have postulated the intermediacy of a transition metal complexed carbene–transition metal bonded carbonium ion hybrid as a mechanistic bridge between the starting bicyclo[1.1.0]butanes and the diene products. This mechanistic hypothesis stood in stark contrast to the postulate of concerted cleavage of the side bonds of the bicyclo[1.1.0]butane derivatives initially presented for the silver ion catalyzed rearrangements of these systems.³¹ Both our results² and those of Masamune's group³² demonstrated that a concerted mechanism was untenable. This led to the abandonment of the "direct symmetry disallowed [$\sigma 2_s + \sigma 2_s$] bond reorganization" theory, even by its originator.³³ More recently, the silver ion catalyzed rearrangement of simple bicyclo[1.1.0]butane derivatives has been postulated to occur *via* an "argento carbonium ion."³³ Obviously, the "argento carbonium ion" is merely one of the resonance contributors of the resonance hybrid transition metal complexed carbene–transition metal bonded carbonium ion initially postulated by us.² The fact that only part of our concept has been adopted for the silver ion catalyzed rearrangements of bicyclo[1.1.0]butanes raises the question of whether the transition metal complexed carbene represents an important resonance contributor to the resonance hybrid intermediate. We feel that the recent intramolecular trapping of the "carbenoid" intermediate observed in our laboratory for rhodium complex promoted rearrangements of phenyl-substituted bicyclo[1.1.0]butanes³⁴ and the exquisite intermolecular trapping of a "carbenoid" type intermediate in the nickel complex promoted cleavage of **3** by Noyori and coworkers³⁵ provide overwhelming

(30) It could be argued that the conversion of **30** into **7** might proceed *via* conversion of **24** ↔ **25** into **6** and subsequent isomerization of **6** into **7**. We feel this suggestion is made unlikely by the essentially quantitative nature of the conversion of **30** into **7**. This follows because the conversion of homoallylic diazo compounds into derivatives of bicyclo[1.1.0]butane is generally a relatively low-yield process^{16c} and the transition metal promoted isomerization of **6** into **7** is itself less than quantitative.

In principle, it should be possible to establish that the conversion of **30** into **7** does not proceed *via* the formation of **6** as an intermediate. This would require that **30** be doubly isotopically labeled. In practice, the synthesis of the necessary labeled version of **30** and the analysis of the resultant labeled version of **7** would be prohibitively difficult.

(31) L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *J. Amer. Chem. Soc.*, **92**, 7002 (1970); L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, **93**, 1288 (1971).

(32) M. Sakai and S. Masamune, *ibid.*, **93**, 4610 (1971); M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, **93**, 4611 (1971).

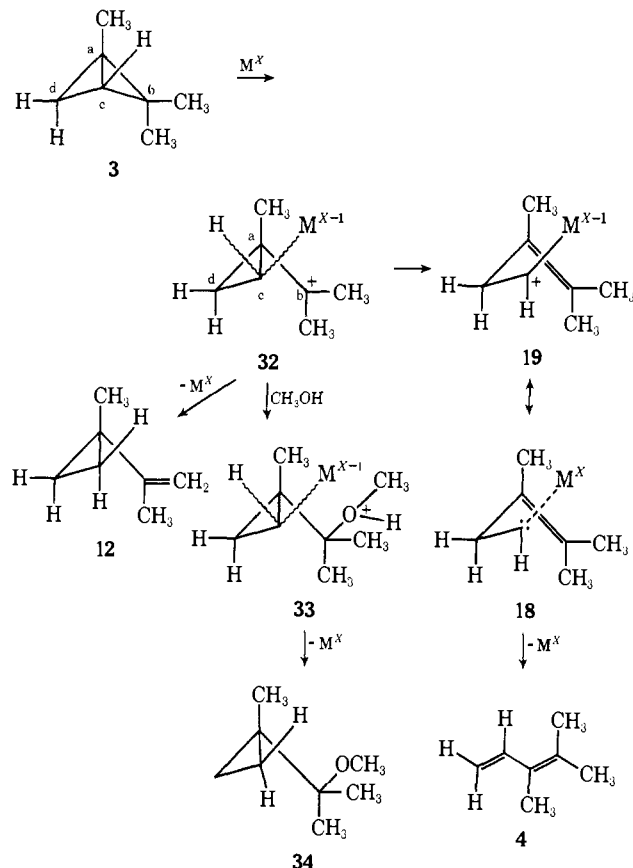
(33) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971).

(34) P. G. Gassman and T. Nakai, *ibid.*, **93**, 5897 (1971); the synthesis of azulenes reported in this communication has been found to be fairly general.

(35) R. Noyori, T. Suzuki, Y. Kumagai, and H. Takaya, *ibid.*, **93**, 5894 (1971). The complex and unusual properties of the intermediate generated in this reaction are evident from its facile addition to the electron deficient double bond of the acrylate ester, and its failure to add to the other olefins present in solution. This indicates that the metal complexed intermediate generated in the nickel(0) promoted rearrangement has some nucleophilic character. This indicates to us that in the nickel(0) studies back donation of electrons may make the "carbenoid" intermediate take on properties similar to ylides.

evidence for the carbenoid character of the intermediate. Since this finding holds for both rhodium and nickel complexes, we anticipate that it will also apply to many other metal complexes.

The major question which remained to be answered as part of this study concerned the detailed process whereby the transition metal complexed carbene-transition metal bonded carbonium ion was formed from the bicyclo[1.1.0]butane nucleus.³⁶ The formation of both diene (**4**) and vinylcyclopropane (**12**) from **3** suggested to us that a common intermediate might possibly be involved as a precursor of both **4** and **12**. Such an intermediate would also have to qualify as a precursor of the resonance hybrid represented by **18** and **19**. An intermediate which would appear to meet all of these requirements is **32**. The

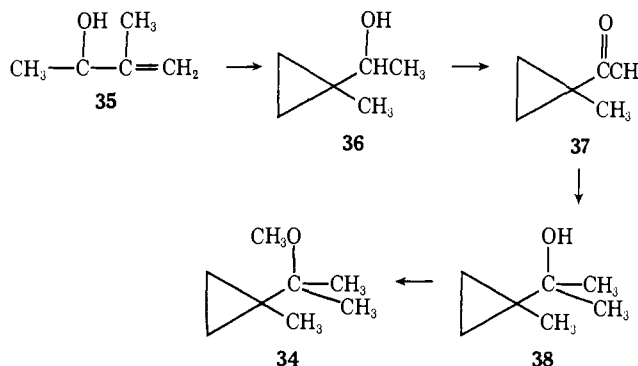


reactions of **32** might be expected to be very different in nonnucleophilic solvents as compared to nucleophilic solvents. In chloroform or acetonitrile, which are the common solvents used in our transition metal promoted rearrangements of strained ring systems, an intermediate such as **32** would be expected to either transfer a proton with loss of the metal complex to give the vinylcyclopropane **12** or cleave a second bond to produce the **18**–**19** hybrid, which on hydrogen transfer and loss of the metal complex would yield **4**.

In order to establish the intermediacy of a species represented by **32** we switched to the relatively nucleophilic solvent methanol in the hope of trapping **32** prior to further rearrangement. When 2 mol % of rhodium dicarbonyl chloride dimer was added to a methanolic solution of **3** at 25°, a vigorous reaction ensued which yielded 97% of **34** after 1 min. This

(36) For a preliminary report related to part of this problem see P. G. Gassman and F. J. Williams, *Chem. Commun.*, 80 (1972).

reaction was qualitatively more vigorous than the corresponding reaction of **3** with a comparable concentration of the same metal complex in chloroform. The structure of **34** was established on the basis of comparison of its ir and nmr spectra and vpc retention times with those of an authentic sample. The independent synthesis of **34** involved Simmons–Smith addition to 3-methyl-3-buten-2-ol (**35**) to give **36**.



Jones oxidation of **36** gave 1-acetyl-1-methylcyclopropane (**37**). The physical constants of both **36** and **37** correlated quite well with those previously reported in the literature.³⁷ Addition of methyl lithium to **37** produced the tertiary carbinol **38**³⁸ which was converted to the alkoxide with sodium hydride followed by alkylation with methyl iodide to give **34**.

In principle, the formation of **34** corresponds to the acid-catalyzed addition of methanol to **3**. Thus, a major concern was associated with the possible formation of hydrochloric acid from the reaction of the rhodium dicarbonyl chloride dimer with methanol, followed by "simple" acid-catalyzed addition of methanol to **3**. Several control experiments were necessary in order to eliminate the possibility of a protic acid controlled reaction.^{38a} First, we found that rhodium dicarbonyl chloride dimer could be recovered unchanged from methanol after 1 min at 25° in the absence of **3**. Secondly, we prepared and rigorously purified³⁹ rhodium dicarbonyl acetylacetonate.⁴⁰ Use of this

(37) M. Julia, R. Guegan, Y. Noël, and T. Song-Yu, *C. R. Acad. Sci.*, 260, 4222 (1965); M. Julia, S. Julia, and Y. Noël, *Bull. Soc. Chim. Fr.*, 1708 (1960).

(38) This alcohol had previously been reported to arise from the acid-catalyzed hydration of **3**.^{12,13}

(38a) NOTE ADDED IN PROOF. Subsequent to the submission of this manuscript, two different research groups published low-temperature nmr spectral data on intermediates formed in the transition metal complex promoted rearrangement of bicyclo[1.1.0]butane derivatives [S. Masamune, M. Sakai, and N. Darby, *Chem. Commun.*, 471 (1972); W. G. Dauben and A. J. Kielbania, Jr., *J. Amer. Chem. Soc.*, 94, 3669 (1972)]. We were pleased to see that both of these groups interpreted their spectral data in terms of a metal-complexed carbene intermediate or its resonance form, the transition metal bonded carbonium ion.

Although Dauben and Kielbania agreed with our concept of a metal-complexed carbene, they disagreed with our suggested origin of this intermediate. Their comments prompted a reinvestigation of our studies in methanol. We have found that under special conditions a very acidic media can be generated from methanol, rhodium dicarbonyl chloride dimer, and **3**, even in the presence of base. The results obtained in our laboratory [P. G. Gassman and R. Reitz, unpublished work] show that the overall picture is more complex than either we or Dauben and Kielbania have indicated. Although we now conclude that acid-catalyzed addition of methanol can occur under our conditions, we wish to note that we cannot accept either a portion of Dauben and Kielbania's experimental results or mechanistic conclusions relative to that aspect of our work involving methanol. Our detailed study of this complex chemistry will be the subject of a future report.

(39) This catalyst was prepared from rhodium dicarbonyl chloride dimer according to literature procedures.⁴⁰ No contamination by the starting material was found using analytical procedures which would have detected considerably less than 1% impurity.

(40) F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 3156 (1964).

rhodium complex with **3** in chloroform gave 58% of **4** and 11% of **12**. In methanol, rhodium dicarbonyl acetylacetonate (**39**) promoted the conversion of **3** into **12** (13%) and **34** (84%). To ensure the complete absence of protic acid, an amount of sodium methoxide equivalent to 10% of the rhodium dicarbonyl acetylacetonate was added to a methanolic solution of **39**. This very basic solution of **39** gave the same results on reaction with **3** as was previously observed in the absence of sodium methoxide.⁴¹ These experiments established that it was the rhodium complex and not protic acid which was responsible for the conversion of **3** into **34**.^{38a}

The relatively clean conversion of **3** into **34** in the presence of rhodium(I) complexes in methanol supported our suggestion that the transition metal complex promoted rearrangement of simple bicyclo[1.1.0]butanes proceeds by a stepwise process which involves initial cleavage of a side bond to yield the most stable cyclopropyl cation, such as **32**.⁴² Capture of nucleophilic solvent by **32** then produces **33**, which on proton transfer and cleavage of the carbon-metal bond yields **34**. It should be noted at this point that we cannot rigorously exclude the possibility that different mechanisms might be involved in methanol *vs.* acetonitrile or chloroform.

In summary, we have shown that rhodium(I) complexes are capable of promoting the facile rearrangement of simple derivatives of bicyclo[1.1.0]butanes. A strong argument can be made that the overall process involves the initial addition of the rhodium complex to the strained bicyclic in a Lewis acid type reaction to yield a carbonium ion. Depending on the solvent, the substitution, and the catalyst, the reaction can either be quenched at this stage or can undergo further bond cleavage to yield a resonance hybrid of a transition metal complexed carbene-transition metal bonded carbonium ion.

We are continuing to investigate the more intriguing synthetic and mechanistic aspects of these interesting transition metal complex promoted reactions.

Experimental Section⁴³

Pyrolysis of 2,2,4,4-Tetramethylbicyclo[1.1.0]butane^{14,44} (**6**). All glassware used in this experiment was washed thoroughly with

(41) Control experiments demonstrated that both pure methanol and methanolic sodium methoxide added slowly to **3** to give **34**. However, these reactions were much too slow to account for our results. For instance, at 25° methanolic sodium methoxide had converted **3** into **34** to an extent of less than 15% after 24 hr. It should be noted that we have not rigorously established that the reactive species is rhodium dicarbonyl chloride dimer in methanol. In principle, a rapid equilibrium between the rhodium(I) complex, methanol, and some new complex could exist. If removal of the methanol should shift such a hypothetical equilibrium back to the starting rhodium(I) complex, a new complex (in equilibrium) would have gone undetected.

(42) This hypothesis is also supported by the experimental observation that 1,3-dimethylbicyclo[1.1.0]butane, which would have to yield a primary carbonium ion *via* our suggested mechanism, reacts orders of magnitude more slowly than **3** with rhodium(I) complexes: P. G. Gassman and G. R. Meyer, unpublished results. These results would tend to diminish but not completely exclude the possibility that the center C₁-C₃ bond cleaved first, followed by a rapid cyclobutyl-cyclopropylcarbonyl cation type rearrangement.

(43) Melting points and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord. Ultraviolet spectra were obtained on either a Cary 14 or Cary 15 recording spectrophotometer. Nmr spectra were recorded on either a Varian Associates A-60-A or HA-100 spectrometer and reported in τ units relative to tetramethylsilane ($\tau = 10.00$) as the internal standard. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

(44) We wish to thank Dr. G. R. Meyer for performing this experiment.

ethereal ammonia and oven dried prior to use. A 0.5-g sample of **6**¹⁴ was added dropwise to a tube 30 × 2 cm which was packed with glass beads and heated to 380° while the tube was being swept with dry nitrogen at the rate of 60 ml/min. The product from the pyrolysis was condensed and trapped in a series of traps cooled to -78°. The product was shown to be homogeneous by vpc analysis. The ir and nmr spectra of the pyrolysis product were shown to be identical with a commercial sample of 2,5-dimethyl-2,4-hexadiene (**7**).²⁵

1,2,2-Trimethylbicyclo[1.1.0]butane (3). Compound **3** was prepared following the literature procedures of Skattebøl¹² and Moore and coworkers.¹³

Rearrangement of 3 Promoted by Rhodium Dicarbonyl Chloride Dimer⁴⁵ in Chloroform. A solution of 241 mg (2.5 mmol) of **3** in 3 ml of chloroform was cooled to 0° and 28.5 mg (0.07 mmol) of rhodium dicarbonyl chloride dimer was slowly added. An immediate exothermic reaction was observed and the solution turned brown. The reaction mixture was allowed to stand at 25° for 3 hr; then the solvent and products were vacuum transferred away from the transition metal complex. Nmr spectral analysis established the complete absence of starting **3** at this time. The two-component product mixture was separated into pure fractions of **4** and **12** by preparative vpc utilizing a 20% D.C. Silicone Fluid No. 200, 1000 cs on a 60-80 Columpak column (10 ft × 1/4 in.) at 70°.

The first component to elute showed an infrared absorption consistent with the presence of a terminal methylene. In addition, this compound had absorptions in the nmr (CCl₄) at τ 9.59 (2 H, br s), 9.33 (2 H, br s), 8.81 (3 H, s), 8.30 (3 H, s), and 5.23 (2 H, m). On the basis of the spectral evidence, this component was assigned structure **12**. Confirmation of this assignment was provided by comparison with an authentic sample of **12** prepared according to the literature procedure^{12,13} *via* the acid-catalyzed isomerization of **3**.

The second component to elute was assigned structure **4** on the basis of its spectral properties. The ir spectrum showed peaks at 6.10 and 6.24 μ , characteristic of a conjugated diene, and the presence of a strong absorption at 11.18 μ , indicating the presence of a terminal methylene unit. The nmr spectrum showed two overlapping singlets at τ 8.26 and 8.22 (9 H), a 1 H doublet centered at 5.10 ($J = 11$ Hz), a 1 H doublet at 4.95 ($J = 17$ Hz), and a 1 H doublet of doublets centered at 3.20 ($J = 17, 11$ Hz). The uv spectrum of **4** had λ_{\max} (95% ethanol) 238 nm (ϵ 18,580) characteristic of a conjugated diene. Finally, a small sample of **4** was hydrogenated over 5% Pd/C to yield 2,3-dimethylpentane, which was identical with a commercial sample.²⁵

In order to determine the yields of **4** and **12** the reaction was repeated with two modifications; the reaction was run for only 5 min, and the analysis was made by vpc on a 10 ft × 1/8 in. column packed with 20% D.C. Silicone Fluid No. 200, 1000 cs on a 60-80 Columpak at 95°, using 2,2,4-trimethylpentane as an internal standard. Under the conditions detailed **3** gave 30% of **12** and 58% of **4**.⁴⁶

1,1,2-Trimethyl-3-deuteriobicyclo[1.1.0]butane (13). A solution of ethereal *n*-butyllithium (54 ml containing 41.6 mmol of *n*-butyllithium), 4.86 g of tetramethylethylenediamine, and 10 ml of ether was stirred for 10 min under a dry nitrogen atmosphere. A solution of 2 g of **3** (20.8 mmol) in 5 ml of anhydrous ether was added dropwise and the solution was stirred at room temperature for 6 hr. The reaction mixture was then hydrolyzed *via* dropwise addition of deuterium oxide, followed by stirring for 10 hr. The inorganic salts were removed by filtration and washed thoroughly with anhydrous ether. The combined ethereal solutions were washed with saturated sodium chloride and dried over anhydrous potassium carbonate. The solution was concentrated by distillation of the ether and the product was separated from the remaining ether by preparative vpc on a 10% Carbowax 20M-KOH on 60-80 Chromosorb W column at 25°. The nmr spectrum of **13** was very similar to that of **3** except for a sharpening of the absorption at τ 9.22.

Reaction of 13 with Rhodium Dicarbonyl Chloride Dimer. The reaction of **13** with rhodium dicarbonyl chloride dimer was carried out in chloroform exactly as has been described above for **3** to yield **15** and **16**. The nmr spectra of **15** are described in detail in the main body of this paper. The spectra of **15** and **16** indicated that **13** had been labeled with deuterium to the extent of $82 \pm 3\%$. The

(45) The rhodium dicarbonyl chloride dimer used in this study was purchased from Strem Chemicals Inc., Danvers, Mass.

(46) A similar reaction carried out in acetonitrile as solvent gave 4% of **12** and 33% of **4**.

nmr spectrum of **16** showed peaks at τ 9.59 (1.1 H, br s), 9.33 (2 H, br s), 8.81 (3 H, s), 8.30 (3 H, s), and 5.23 (2 H, m).

1,2,2,3-Tetramethylbicyclo[1.1.0]butane (20). Utilizing the procedure of Moore and coworkers,¹⁸ 4 g of **3** was treated with butyllithium, followed by methyl iodide to yield 3.20 g (70% yield) of **20**, bp 105–110°.

Rhodium Dicarbonyl Chloride Dimer Promoted Isomerization of 20. A solution of 750 mg of **20** in 5 ml of chloroform was cooled to 0° and 135 mg of rhodium dicarbonyl chloride dimer was slowly added. An immediate exothermic reaction occurred and the solution turned dark red-brown. After standing for 10 hr the volatile material was vacuum transferred away from the transition metal complex at 25° and 0.3 mm. Two major products were isolated from the chloroform solution by preparative vpc on a 20% D.C. Silicone Fluid No. 200, 1000 cs on a 60–80 Columeck column (9 ft \times 1/4 in.) at 80°.

The first component to elute had ir absorptions at 6.08 (C=C), 7.30 (CH₃), and 14.06 μ (cis disubstituted olefin). Its nmr spectrum showed peaks at τ 4.63 (1 H, m, $J_{AB} = 11$ Hz, $J_{A-CH_3} = 6.5$ Hz) and 4.12 (1 H, d, $J_{AB} = 11$ Hz). The ultraviolet spectrum showed λ_{max} (2,2,4-trimethylpentane) 220 nm (ϵ 3850) characteristic of a twisted diene.⁴⁷ The mass spectrum showed a parent peak at m/e 110. On the basis of this spectral evidence this component was assigned structure **21**.²⁴ A small sample of **21** was catalytically hydrogenated over 5% Pd/C to give 2,3-dimethylhexane which was spectroscopically identical with a commercial sample.²⁵

The second component to elute had ir peaks at 6.04 and 6.23 (C=C, conjugated diene), 7.26 (CH₃), and 10.42 μ (trans disubstituted olefin). The nmr spectrum showed absorptions at τ 4.54 (1 H, m, $J_{AB} = 15$ Hz, $J_{A-CH_3} = 6.5$ Hz), 3.56 (1 H, d, $J_{AB} = 15$ Hz). The ultraviolet spectrum of this component showed λ_{max} (2,2,4-trimethylpentane) 240 nm (ϵ 17,750) [lit.²⁴ λ_{max}^{EtOH} 240 nm (ϵ 20,700)]. Mass spectroscopy gave a parent ion at m/e 110. On the basis of this spectroscopic evidence the second component was assigned structure **22**,²⁴ n^{25D} 1.4790 (lit.²⁴ n^{25D} 1.4752). Reduction of a small amount of **22** over 5% Pd/C gave 2,3-dimethylhexane which was identical in all respects with an authentic sample.²⁵

Yields were determined by vpc analysis on a 10 ft \times 1/8 in. 20% D.C. Silicone Fluid No. 200, 1000 cs on a 60–80 Columeck column at 100°, using 2,2,4-trimethylpentane as an internal standard. The analytical runs were carried out exactly as described for the preparative run, except that the products were not vacuum transferred. In this way it was found that **20** gave a 46% yield of **21** and a 50% yield of **22**.

In control reactions, pure samples of both **21** and **22** were treated with rhodium dicarbonyl chloride dimer under the reaction conditions for 12 hr. Both **21** and **22** were recovered unchanged from these control reactions, demonstrating that the observed mixture did not arise *via* isomerization of either component.

(*E*)-1,2-Dimethyl-1-(2-propenyl)cyclopropane (**23**)²⁷ was also exposed to the reaction conditions for 1.5 hr.⁴⁴ Again no isomerization to either **21** or **22** was observed.

2,2,4,4-Tetramethylbicyclo[1.1.0]butane (6). The highly symmetrical compound **6** was prepared in three steps from 2,2,4,4-tetramethyl-1,3-cyclobutanedione (dimethylketene dimer) following literature procedures.¹⁴

Rhodium Dicarbonyl Chloride Dimer Promoted Isomerization of 6. A solution of 200 mg of **6** in 2 ml of chloroform was cooled in an ice-water bath and 36 mg (5 mol %) of rhodium dicarbonyl chloride dimer was added. An immediate exothermic reaction took place and the solution turned a pale yellow. After setting at 25° for 10 hr, the volatile material was vacuum transferred at 25° and 0.3 mm to separate it from the transition metal complex. This chloroform solution was shown to contain only one component by vpc analysis. An nmr spectrum of the chloroform solution was identical with the nmr spectrum of a chloroform solution of commercial 2,5-dimethyl-2,4-hexadiene (**7**). A sample of **7** was purified by preparative vpc on the same preparative column used in the purification of **21** and **22**. This material was shown to have an infrared spectrum identical with the authentic sample. An 83% yield of **7** was obtained as determined by vpc analysis using 2,2,4-trimethylpentane as an internal standard.

2,2,4-Trimethylpent-3-enal (28). The aldehyde **28** was prepared according to the literature procedure²⁹ with the modification that

the dimethylketene dimer **26** was reduced to **27** with lithium aluminum hydride rather than catalytically. This represented a distinct improvement over the literature process.

Tosylhydrazone of 2,2,4-Trimethylpent-3-enal (29). To a stirred solution of 1.26 g of **28** in 5 ml of dry methanol was added dropwise a solution of 1.86 g of *p*-toluenesulfonyl hydrazine in 20 ml of methanol. The solution was refluxed for 5 hr. The solution was cooled and concentrated to ca. 12 ml. Water was added dropwise until precipitation began to occur. The solution was cooled to –70° and the white precipitate which formed was collected by filtration, washed with cold methanol, and dried to give 2.20 g (75% yield) of **29**, mp 109–110°.

Two recrystallizations from methanol gave an analytical sample, mp 110–112°.

Anal. Calcd for C₁₅H₂₂N₂O₂S: C, 61.19; H, 7.53; N, 9.51; S, 10.89. Found: C, 60.92; H, 7.50; N, 9.54; S, 10.78.

4-Diazo-2,2,4-trimethylpent-2-ene (30). A solution of 2.1 g of **29** in 15 ml of tetrahydrofuran was cooled to 0–5° under a nitrogen atmosphere and 5 ml of a 1.6 *N* solution of *n*-butyllithium in hexane was added dropwise over a 5-min period. A white precipitate formed almost immediately. The solution was stirred for an additional 0.5 hr and the tetrahydrofuran was removed under vacuum. The residual salt was transferred to a vacuum line and the system was evacuated to 0.003 mm. The flask containing the salt was gradually heated to 85–90° and the diazo compound **30** was collected in a trap kept at –70°. This material, which was contaminated by a small amount of tetrahydrofuran, was shown to be otherwise pure within the limits of analysis by ir and nmr spectroscopy. No trace of 2,5-dimethyl-2,4-hexadiene could be detected by either ir or nmr as a contaminant in **30**. Due to the thermal instability of **30**, no attempt was made to further purify the sample.

Rhodium Dicarbonyl Chloride Dimer Promoted Decomposition of 30. A weighed aliquot of the mixture of **30** and tetrahydrofuran was diluted with chloroform and a small amount (ca. 5 mg) of rhodium dicarbonyl chloride dimer was added. An immediate vigorous evolution of nitrogen ensued. When nitrogen evolution ceased isooctane was added as an internal standard and the solution was analyzed by vpc on a 10 ft \times 1/8 in. 20% D.C. Silicone Fluid No. 200 on Chromosorb P column at 75°. Within the limits of analysis by vpc, **30** had decomposed to give only **7**. The yield of **7** was 56% based on **29**.

A preparative scale reaction was carried out and the single product was collected by preparative vpc and shown to be identical in all respects with 2,5-dimethyl-2,4-hexadiene (**7**).

Rhodium Dicarbonyl Chloride Promoted Methanolysis of 3. To a solution of 300 mg of **3** in 3 ml of methanol at 25° was added 11 mg of rhodium dicarbonyl chloride dimer. An immediate extremely vigorous exothermic reaction occurred. After 1 min no trace of **3** could be detected by vpc analysis. Using *n*-butyl alcohol as an internal standard it was demonstrated by vpc analysis that **3** was converted to **34** in 97% yield. The material formed in this reaction was shown to be identical in all respects with an independently synthesized sample of **34**.

1-Acetyl-1-methylcyclopropane (37).³⁷ This known compound was prepared *via* treatment of 3-methyl-3-buten-2-ol with methylene iodide-Zn(Cu) couple, followed by Jones oxidation.

(1-Methylcyclopropyl)dimethylcarbinol Methyl Ether (34). To a 2-g sample of **37** in 20 ml of anhydrous ether was added dropwise an ethereal solution containing 1.25 equiv of methyllithium. The dropping rate was controlled in order to maintain a gentle reflux. After stirring for 2 hr, the reaction mixture was hydrolyzed through the addition of excess water. The layers were separated and the aqueous phase was washed thoroughly with ether. The combined ethereal phases were washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solution was concentrated to yield the crude tertiary alcohol **38**. This material was shown to be identical with the material obtained by acid-catalyzed hydration of **3**, according to the literature procedure.¹²

The crude alcohol was stirred for 1 hr at reflux in 25 ml of tetrahydrofuran containing 1.63 g of 60% sodium hydride in mineral oil. A solution of 5.8 g of methyl iodide was added dropwise and the reaction mixture was stirred overnight. Water was added to dissolve the salts which had precipitated. The layers were separated and the aqueous layer was washed thoroughly with ether. The combined ethereal solutions were washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the ether was carefully distilled. Distillation of the residue gave 1.76 g (67%) of **34**, bp 80–81° (115 mm).

(47) *cis,cis*-1,3-Cyclooctadiene shows λ_{max} (isooctane) 228 nm (ϵ 4300). We wish to thank Dr. E. Williams for providing this information. On the basis of Woodward's rules, **21** should have λ_{max} 237 nm if a planar conformation were possible.

An analytical sample of **34** was collected by preparative vpc on a 19% Carbowax 20M Chromosorb W column at 70°, n_D^{20} 1.4218.

Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.77; H, 12.56.

Rhodium Dicarbonyl Acetylacetonate (39). This complex was prepared according to the procedure of Bonati and Wilkinson.⁴⁰ It was shown by mass spectrometry that the material was at least 99% pure.

Treatment of 3 with 39 in Chloroform. A chloroform solution of **3** was treated with 2 mol % of **39** utilizing the same general experimental procedure described above for the reaction of **3** with rhodium dicarbonyl chloride dimer. Analysis of the product mixture by vpc indicated the formation of 58% of **4** and 11% of **12**.

Treatment of 3 with 39 in Methanol. The same general procedure

was used in this experiment as has been previously outlined for the reaction of **3** with methanol in the presence of rhodium dicarbonyl chloride dimer. The major difference in the two reactions was that **39** caused a somewhat slower reaction. Vpc analysis of the products from this reaction indicated the formation of 84% of **34** and 13% of **12**.

Addition of an amount of sodium methoxide equivalent to 10% of the amount of **39** caused no perceptible change in the reaction. The yields of **34** and **12** remained the same.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

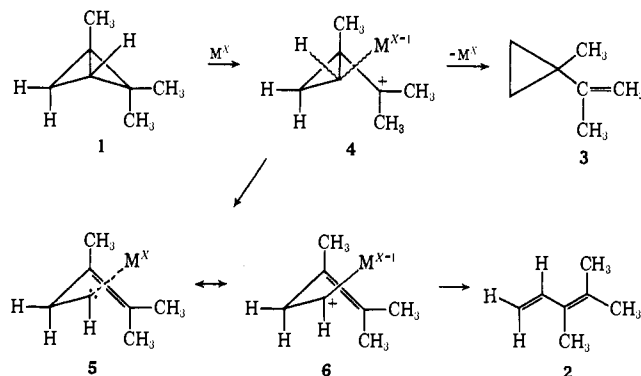
Transition Metal Complex Promoted Rearrangements. The Effect of the Metal and of the Attached Ligands on the Mode of Cleavage of Methylated Bicyclo[1.1.0]butanes¹

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Abstract: A study has been carried out in order to determine the effect of the metal, of the oxidation state of the metal, and of the ligands attached to the metal, in the transition metal complex promoted isomerization of methyl-substituted bicyclo[1.1.0]butanes. The results of these studies have been compared to our results with derivatives of rhodium(I). We found that derivatives of chromium, cobalt, copper, gold, iridium, manganese, mercury, palladium, platinum, rhenium, rhodium, ruthenium, tin, and zinc promoted the isomerization of methylated bicyclo[1.1.0]butanes. The nature of the products formed was dependent on the metal, the oxidation state of the metal, and on the ligands attached to the metal. The dependency on the attached ligand was amply demonstrated by the formation of different products (resulting from the cleavage of different bonds) when bisbenzotriple palladium(II) chloride was replaced by π -allylpalladium(II) chloride dimer. The mechanisms of these isomerizations are discussed. A stepwise process of bond cleavage is suggested. In general, insufficient evidence prohibits any definitive explanation of the specificity of the various metal derivatives which we have used in our investigation of the transition metal promoted isomerization of bicyclo[1.1.0]butane derivatives.

In the preceding paper¹ we have discussed in detail the rhodium dicarbonyl chloride dimer promoted isomerizations of methylated bicyclo[1.1.0]butane derivatives. We presented evidence in support of an overall mechanism which is shown below for the conversion of 1,2,2-trimethylbicyclo[1.1.0]butane (**1**)



into a mixture of **2** and **3**. We suggested that the transition metal complex behaves initially as a very specific Lewis acid type species, which attacks the bicyclo-

[1.1.0]butane moiety, producing cleavage of a side bond to give the most stable cyclopropylcarbanyl cation (**4**). Proton transfer and loss of the metal would then explain the formation of **3**.² An alternate mechanistic path, which **4** could follow, would involve cleavage of the central bond to yield a resonance hybrid represented by the transition metal complexed carbene **5** and the transition metal bonded carbocation **6**. Again, hydrogen transfer and loss of the metal complex would give the observed product **2**.² In view of the extremely unusual nature of these rhodium dicarbonyl chloride dimer promoted rearrangements, we decided to investigate the use of derivatives of other transition metals in the rearrangement of derivatives of bicyclo[1.1.0]butane. We now wish to present the details of this investigation.⁴⁻⁷

(2) Ample precedent exists for the protonolysis of carbon-metal bonds.³ We feel that it may be possible for this protonolysis to occur *via* initial proton transfer from carbon to metal and then from metal to carbon. We are currently investigating this aspect of these rearrangements.

(3) For a recent leading reference see T. J. Katz and S. A. Cerefece, *J. Amer. Chem. Soc.*, **93**, 1049 (1971); see also M. Orchin, *Advan. Catal.*, **16**, 1 (1966).

(4) For preliminary reports of part of this work see P. G. Gassman and F. J. Williams, *Tetrahedron Lett.*, 1409 (1971); P. G. Gassman, T. J. Atkins, and F. J. Williams, *J. Amer. Chem. Soc.*, **93**, 1812 (1971); P. G. Gassman, G. R. Meyer, and F. J. Williams, *Chem. Commun.*, 842 (1971).

(1) Paper XXXIII of a series on The Chemistry of Bent Bonds. For the previous paper in this series see P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **94**, 7733 (1972).